

particular concern for the development of lithium accumulators. In this connection, it is very important to determine some of the dynamic characteristics of the lithium/non-aqueous electrolyte interface and to learn what governs these characteristics.

An equivalent circuit of systems studied is proposed. The parameters of the circuit were determined in different electrolytes by a grapho-analytical method based on impedance measurements. Experimental data were compared with the results of mathematical modelling of various equivalent circuits. The analysis carried out allows us to suggest the location of the growth zone of a passivating film and to a certain degree to predict a system's behaviour and its dynamic properties.

Changing the composition, volume and surface of binary and ternary lithium alloys allows us to change significantly the parameters of the passivating film, which affects both system storage and cycling efficiency.

P12

Lithium cobaltite. A supplier's point of view

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This paper reviews different aspects linked with the production of LiCoO_2 and its use as cathode material in secondary lithium batteries. As the electrochemical performances of LiCoO_2 are now well established, the poster focusses on other aspects that have been less addressed in the past.

Correlations between particle size, surface area and tap densities are presented. The influence of the conditions of synthesis and of the nature of the starting products on these properties are also discussed.

In a second part of the poster, economic aspects are reviewed. The structure of the cost of LiCoO_2 is shown and compared to that of other lithiated oxides.

Forecasts are given for total production, share of each type of oxide and market price.

P13

Analysis of lithium manganese oxide for lithium rechargeable batteries

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Introduction

Lithium manganese oxide (LiMn_2O_4) is the favoured cathode material in the long term for lithium rechargeable batteries because it can be produced from cheap and readily available starting materials and it is non-toxic. At present, lithium cobalt oxide is used in rechargeable lithium-ion batteries but is expensive and somewhat toxic. However the synthesis of LiMn_2O_4 , particularly in large quantities, is difficult to control, as there are many different chemical phases in the lithium/manganese/oxygen system. This led to difficulty in specifying LiMn_2O_4 , as nominally similar materials in practice show very different performance in batteries.

A programme of analyses has been carried out to characterise lithium manganese oxide using a range of techniques. Both commercial samples and materials we have synthesised have been analysed for lithium and manganese content by ICPAES (inductively coupled plasma atomic emission spectrometry), oxygen content by a LECO TC436 analyser and by thermogravimetric analysis. The valence state of manganese was determined by a titration method following reductive dissolution of iron (II) sulfate in sulfuric acid solution. X-ray diffraction patterns were used to monitor the presence of impurities.

Results

The results obtained indicate that samples of lithium manganese oxides prepared at lower temperatures are the so called oxygen-rich, defect spinel and those prepared at higher temperatures contain less oxygen and have formulae closer to those of the regular stoichiometric spinel. Furthermore, the LECO oxygen analyser gave poor results because this technique is only suitable for trace amounts of oxygen in alloys; the classical titration method gave better results for oxygen content. The average oxidation state of Mn in LiMn_2O_4 was found to be about 3.55 for samples examined. X-ray powder diffraction analyses of the prepared powders indicated a spinel structure with less impurities (LiMn_2O_4) at higher temperatures. The amount of these impurities appeared to increase with decrease in the calcining temperatures. In addition, the diffraction peaks were broader in the samples calcined at lower temperatures. Particle size characterisation of LiMn_2O_4 was carried out by a sieving technique and by a laser diffraction method. The results obtained by the two methods were very similar, but the spinel oxides calcined at higher temperatures have smaller surface area. The results discussed above are in agreement with previous findings, all relevant evidence for the above results being shown on the poster.

Conclusion

In summary it is difficult to control the reaction parameters such as uniform temperature, cooling time and oxygen flow

rate to make a spinel (LiMn_2O_4) with predetermined stoichiometry. X-ray diffraction cannot readily distinguish the different phases of lithium manganese oxide. The manganese and lithium analyses carried out by ICPAES in duplicate are in good agreement. It was observed that the oxygen contents of spinel samples fall with increasing temperature and also the particle size results are in good agreement for the sieving technique and for the laser diffraction method. Furthermore, spinels prepared at 850°C appear to be in good agreement with the values on the J.C.P.D.S. card.

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P14

Development of a lithium-ion polymer battery for space power applications

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Introduction

In recent years lithium-ion batteries [1] have emerged as the leading advanced power source for a range of applications. Driven by the demands of the portable consumer market, small lithium ion cells are now available commercially and have demonstrated excellent cycle life and safety characteristics.

Here we report results from a project aimed at developing a lithium-ion polymer battery (LiPB) into a power source for GEO satellites. The LiPB technology combines the cycle life and safety benefits of the lithium-ion chemistry with those of flexible cell geometry afforded by the use of a solid polymer electrolyte. The concept of the all solid state battery is very appealing. Solid state batteries are intrinsically spill proof and rugged, have long shelf-life, and are capable of being engineered into any geometry. LiPB is a laminate structure based on LiNiO_2 as the active cathode material [2] and graphite as the active anode material. The average cell voltage during discharge is about 3.5 V.

Experimental

The composite anode, polymer electrolyte and composite cathode components of LiPB can be easily prepared using a range of coating techniques. Fabrication of LiPB laminate is achieved using a combination of heat and pressure.

Electrochemical evaluations under GEO space power duty cycle were performed on 56 cm^2 LiPB cells using Sycopel charge/discharge equipment.

Results and discussion

LiPB technology demonstrates significantly improved performance compared to our previously reported lithium metal anode polymer system [3]. Over 500 cycles have been obtained to date at 60% depth of discharge under a GEO duty cycle. A comparison with state-of-the-art liquid electrolyte cell technology indicates that lithium-ion chemistry is capable of achieving in excess of 1000 GEO cycles at 80% depth of discharge.

References

- [1] T. Nagaura and K. Tozawa, *Prog. Batteries and Solar Cells*, 9 (1990) 209.
- [2] M. Broussely et al., *J. Power Sources*, 43–44 (1993) 200–216.
- [3] W.J. Macklin et al., in A. Attewell and T. Keily (eds.), *Power Sources 15*, International Power Sources Committee, Crowborough, UK, 1995, p. 315.

P15

Parallel cell arrangements for reserve lithium/sulphuryl chloride batteries

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The aim of this work was to investigate the processes leading to failure of large capacity reserve oxyhalide batteries. Previous work in our laboratories has shown that smaller ($< 600\text{ Wh}$) systems, using thionyl or sulphuryl chloride cathodes, have good reliability and predictable behaviour. However, on scale up to larger sizes, premature failure has been observed. Among the factors most responsible are excessive heat generation, leakage currents and lithium dendrite formation.

We report a part of this work concerned with minimising overall leakage currents and heat output through use of parallel arrangements of cells. Where higher currents are required it has been typical practice to make use of parallel sets of series piles. However, if the cells are coupled in parallel before being placed in series, the overall leakage current and heat output can be reduced.

Batteries of five paralleled strings, each string containing four cells in series, were compared with batteries of twenty, series-connected cells. Results showed that the heat output was some 44% less for the parallel arrangement at 25 mA cm^{-2} . Some other important observations were that, in a set of five parallel cells, the cells discharged at different rates (up to 50 mA cm^{-2} and as low as 10 mA cm^{-2} initially). As the higher rate cells became exhausted their current output reduced and the current output from the other cells increased. This current balancing appears to be beneficial in terms of